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A TECHINICAL PROPOSAL

DEVELOPMENT OF AN ECOLOGICAL WARNING SYSTEM FOR THE DELAWARE BAY

DELAWARE DEPARTMENT OF NATURAL RESOURCES AND ENVIRONMENTAL CONTROL

A MULTIDISCIPLINARY EFFORT

Technical Proposal

for

DEVELOPMENT OF AN ECOLOGICAL WARNING

SYSTEM FOR THE DELAWARE RIVER ESTUARY

A Multi-Disciplinary Effort

Within the

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and Environmental Control

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Desired Starting Date January, 1973

The information and data furnished herein shall not be disclosed to third parties or be duplicated, used, or disclosed in whole or in part for any purpose other than to evaluate this proposal.

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Abstract

This three-year joint study of the Delaware River estuary by Delaware's Department of Natural Resources and Environmental Control will develop an "Ecological Warning System." The purpose of such a system is to ultimately provide a reliable surveillance system which will indicate significant variation of pollutant concentrations from the norm and thereby act as a warning system in the long-range. Selected for this demonstration is the concentration variation of seven heavy metals and other pollutants entering and/or within the estuarine system, and the entry of these materials into the human food chain. The extent of contaminant concentration in the estuarine system will be established, based on input-output information derived from sample analyses of the air, soil, water, benthos, and indicator organism, i.e., the Atlantic oyster, <u>Crassostrea virginica</u>. This research program will develop models (both statistical and compartmental) to link the system parameters. The methodology thus developed could be used for other contaminants having access to the system, and for the system per se.

Keywords: Delaware River, Ecological Warning System, Estuary, Heavy Metals, Model, Pollutants, Oysters

Acknowledgements

Thanks are due to Dr. Henry Tingey of the University of Delaware and Hydroscience, Inc., for their assistance in developing the sections on statistical and predictive modeling, respectively. Thanks also are due Eugene DeMichele of the University of Delaware for editing this proposal.

I SUMMARY

I. Summary

This research program will be a multi-disciplinary approach to develop the methodology for the establishment of an Ecological Warning System. The concentrations of heavy metals entering and/or within the estuarine system have been selected as the mechanism for this development. The extent of contaminant concentration in the estuarine system will be established, based on input-output information derived from air, soil, water, benthos, and indicator organism (the Atlantic oyster, Crassostrea virginica) analyses. In addition, an attempt will be made to quantify interactions to trace pollutants with the marine biosphere and to relate these pollutants to Bay hydrology. It is intended that this research program will develop models to link the system parameters into an Ecological Warning System. By this means, it will be possible to predict the impact of pollutants from the air, soil, etc., on the environment, to establish existing levels of pollutants, and to identify those pollutants having the potential to seriously endanger the human food chain. Although an estuarine system is to be used as a "test area," the methodology developed could be applied as well to other systems.

The technical proposal submitted herewith by the Delaware Department of Natural Resources and Environmental Control represents a multi-disciplined effort involving the physical, biological, and chemical expertise presently available within the Department. In addition, the Department has established avenues whereby the expertise of research groups active in the State and

elsewhere may be utilized to provide added advisory guidance and depth to the project. A carefully planned program to fulfill the requirements of this project is presented in detail. Primary emphasis is on a thorough evaluation of the techniques and equipment needed to develop an ecological warning system through the use of an experienced team of researchers. The first-year effort will consist of the development of (a) the methodology needed to evaluate the relative importance of the various system parameters, and (b) statistical and linear mathematical predictive models. Second and third-year extensions of the study will include the development of a more sophisticated predictive mathematical model which will not rely only on the linear kinetic assumptions used for the first-year study. The methodology thus developed may be used for other contaminants having access to the system.

Recognizing the immediate need for these studies, based on the rapidly developing coastal zone areas on the eastern seaboard, the Delaware Department of Natural Resources and Environmental Control is prepared to initiate work on this program immediately on completion of contract negotiations. An experienced team of researchers is available, as are the technical resources of a well-established and renowned laboratory.

The objective of this program will be to develop the methodology for the establishment of an estuarine zone ecological warning system, using the concentration variations of seven heavy metals within the estuarine system. Trace metals, etc., will be measured in the air, soil, water, benthos, and indicator organisms for the proposed study. Correlation between and among system variables will be made statistically. Predictive models then will be developed to evaluate the effects of these pollutants on the eco-system and to relate them to their potential impact on the human food chain.

The program designed to meet these objectives is broken down into five parts:

1. Evaluation of background information to insure maximum utilization of existing data.

2. Design and development of the methodology needed to carry out the proposed study.

3. A thorough field evaluation of the techniques and equipment utilized.

4. Correlation and interpretation of the field results with a view toward developing the preliminary aspects of a mathematical model relating to biological-chemical-hydrological interactions.

5. Specific conclusions and recommendations with respect to assessment of the first years data and the extension of the program.

Model development and the steps to achieve this development are the objectives of this program and will provide the basis for the estuarine zone ecological warning system. The system will permit not only identification and interpretation of abrupt changes but also of more subtle trends within the system. In the event that abrupt changes are detected, appropriate responsible governmental agencies and project funding agencies will be alerted in sufficient time to react effectively and constructively.

If the problem encompasses areas above or below the demonstration system, action can be instituted on a regional basis. If the problem is local, similar constructive corrective measures can be initiated. Likewise, subtle changes, which heretofore have gone undetected, will be identified at an early stage. Such advance notice of an ensuing problem will permit similar decisive corrective action, based on a sound data base, to be taken by responsible agencies in regard to trends in the estuary.

II INTRODUCTION

II. Introduction

Increasing pollution and public attention to the adverse effects of water and air pollution has led to the need for a better understanding of the economic importance and environmental impact of pollution on coastal zones. Until recently, there had been little concern for the possible effects of pollutional stresses on estuarine systems. High flushing rates coupled with generally low population and industrial densities produced a lack of obvious symptoms of pollution damage. However, some of the effects are subtle, long-term stresses which, until recently, had not been recognized. As population and industrial densities surrounding the estuaries increased, the alteration of the chemical composition of the oceans proceeded at an ever increasing rate. In some instances, the activities of society are increasing the level of pollutants within the system, while in others, ocean-associated materials are being introduced into the estuaries. These activities indeed raise questions of crucial importance that require an in-depth understanding of the consequences of man's chemical invasion of the environment.

The functional responses to man-imposed changes in nature can be detrimental and perhaps there can result the loss or the restricted use of a valuable resource. The ability to predict undesirable results will lead to necessary and protective policies concerning such encroachments.

Objectives of the Proposal

This project involves a multi-disciplinary approach to develop the methodology for the establishment of an estuarine zone ecological warning system. Selected for this demonstration are the concentration variations of seven heavy metals (copper, chromium, zinc, lead, mercury, cadmium, and nickel) within the estuarine system. These pollutants will be measured in the air, soil, water, benthos, and in indicator organisms. The Atlantic oyster, *Crassostrea virginica*, is selected as the indicator organism for this study because of it's commercial important to the Delaware estuary and because of it's availability and physiology (predictive retention and elimination of contaminants based on water quality). The oyster has the capability of magnifying pollutants to concentrations many times greater than that of the water column. Correlation between and among system variables will be made statistically, resulting in a statistical model. Predictive models then will be developed to evaluate the effects of these pollutants on the eco-system and to relate them to their potential impact on the human food chain. The immediate impact of pollution episodes on the ecological system, e.g., heavy metals, chemicals, oils, etc., spilled in the Delaware estuary due to the recent hurricane Agnes, could be assessed temporally and spatially, as well as provide a check on the model designed. The methodology thus developed utlimately will define quantitatively the impact of any waste discharge on an ecologically diverse and economically important marine community.

The system model developed not only will permit identification and quantification but also interpretation of both abrupt and subtle trends in the estuary. The predictive capabilities of the model will avail responsive agencies sufficient opportunity to react with corrective action. Informational input and output from this project will be shared with the funding agency as well as local and federal agencies engaged in pollution abatement/research activities for the purpose of problem identification and suitable action. Data thus collected and analyzed will be made available to other researchers. In like manner, findings by other researchers affecting model limits, parameters, etc., will be incorporated in the Delaware ecological warning system model.

Need for Research

The harmful effects on eco-systems by pollutants resulting from man's activities is causing increasing concern in many areas in the world. Industrial waste contamination of fin fish and shellfish by trace metals, radionuclides, pesticides, herbicides, and petroleum oil has risen sharply during the past decade. Incidents such as methyl mercury in tuna and swordfish, DDT levels in Great Lake salmon, and oil spills in fishing areas has focused scientific attention on the need for efficient methods of continuously monitoring and evaluating all aspects of industrial waste accumulations in the fisheries resources. However, a methodology is required that has the capability of assessing the source and intensity of the pollution effects in any estuary before serious problems evolve. The increasing seriousness of these problems demand that more precise information on the nature and extent of the damage and the pollutants involved be obtained. Before this can be done, however, consistent methods for making such determinations must be developed.

Certain pollutants in sufficient concentration produce immediate toxic effects on the environment. However, the ultimate (and probably more serious) effects of pollution are much more subtle and involve a chain of events which may culminate in the production of undesirable species. To assist in developing more rational environmental standards, methodologies and present system concentrations and their correlations must be evaluated promptly.

Capability of the Department of Natural Resources and Environmental Control for Immediate Action

The personnel assigned to this project will bring with them a broad background of professional experience in marine biology and trace-pollutant analysis, engineering, and hydrology. Their individual capabilities are supported further by the ability to draw on the multi-displinary technical support of an experienced team of researchers in water and air pollution control. This combination of scientific capabilities is necessary to develop an ecological warning system. This proposal, therefore, presents a unique opportunity to obtain data on which to develop a system that will be useful in formulating resource management practices in an area that is currently subject to pollution stress.

III BACKGROUND

III. Background

The estuarine environment is a complex system receiving increasing pollutant discharges in some areas while serving as a recreational or food-culturing resource in other locations. The realized importance of estuarine zones has resulted in world-wide attention directed at marine pollution monitoring to provide data and information on the present levels of contamination and trends. Baseline data on heavy metals, petroleum-derived hydrocarbons, pesticides, etc., and their relationship to the marine (and human) food chain will permit the assessment of these pollutants on the environment. Although comprising but a small percentage of the contaminants in an estuarine-zone system, heavy metals can serve to demonstrate the food-chain relationship within the system.

Heavy Metals in the Hydrosphere

A large number of studies have been devoted to defining the levels of various heavy metals found throughout the hydrosphere. Several investigators found that certain elements increase in concentration with an increase in depth. Ivanoff (1) measured levels of silicon, aluminum, iron, and phosphorus at seven sea stations in the eastern Mediterranean and Tyrrhenian seas and found the metal concentrations to range from 30-to-462, 8-to-224, 4-to-95, and 0-to-38 x 10^{-9} g atom/l, respectively. Barium content ranged from 8-to-14 ug/l in the Pacific (surface-to-deep water, respectively). Other biologically active elements, i.e., silicon, carbon, nitrogen, and phosphorus, also increased with depth. Wolgemuth (2) felt these data confirmed the hypothesis that metals are incorporated into the remains of organisms in the ocean surface and then are released to the deep sea as the organic debris settles toward bottom. Head (3) found that the average molybdenum concentration in sea water from the English Channel and from the northeast Atlantic to be 11.5 and 10.9 ug/l, respectively. Molybdenum, however, has a relatively uniform distribution in sea water with only minor and irregular variation with depth and position.

Water samples were collected during inundation by tides of littoral *Spartina patens* vegetation by Blum (4). Water analysis showed a definite variation with tides in phosphorus, phosphate, and manganese which correspond with changes in the water levels during high tide as well as progressive inundation of *Spartina patens* vegetation. The analysis of tidal waters must take temporal as well as spatial variations into account.

Van Everdingen (5) found high levels of zinc, iron, manganese, and lead in acid spring water. These data were not surprising considering the leaching abilities of acidic substances.

Other groups have collected data on river waters. Schmidt (6) found that the arsenic levels depend on river flow rates while strontium, bromine, rubidium, and barium levels were dependent on industrial waste inflows. Molybdenum, cesium, and zirconium levels depend on the season, while silver and manganese depend on all three factors (river flow, plant loadings, and season).

Basitova (7) found in the southwestern Tadzhikistan that river waters contained manganese, zinc, copper, and molybdenum in the ppb range. Sub-surface waters were found to contain one-fifth the amount of surface-water copper. Voegeli (8) detected molybdenum in 89 percent of Colorado surface water samples. The molybdenum ranged from 1 to 3,800 ug/1.

Porohenskaya (9) found that trace metals in pond bottoms correlated with the content of soils in Ukrainian SSR. Arsenic levels in pelagic sediments averaged 40 mg/1 on a CO_2-free basis; in oceanic rock, arsenic levels are low.

To date, guidelines for metals in marine foods including shellfish is limited to a mercury level of 0.5 mg/1. Only "alert levels" have been established for copper, zinc, cadmium, and chromium. For oysters (Crassostrea), heavy metal alert levels have been prepared by the F.D.A. (Cd, 3.07 mg/1; Pb, 0.94 mg/1; Cr, 1.07 mg/1; Zn, 2,099 mg/1; Cu, 158.3 mg/1; and Hg, 5.0 mg/1). Pringle et al. (10) concluded from their studies of marine mollusks that when the environmental concentration of a particular metal persists over a sufficient period of time, the animal may become physiologically affected and die.

Heavy Metals in the Lithosphere and Atmosphere

Numerous surveys have been conducted to define heavy metal concentrations in the atmosphere (11). Likewise, numerous specialized studies limited to local pollution fallout have been undertaken defining the heavy metal contributions to the soils surrounding certain industries (12). Studies such as the Northeast Soils Survey (13) sponsored by the USDA provide information on the heavy metal concentrations in soils in the northeastern United States. However, virtually no effort has been devoted to defining the

TABLE I. -- Comparison of Lake Sediments with Watershed Soils

Site	C %	N %	C/N	P(mg/kg) Total	P(mg/kg) Aval
Lake Sediments					
Pinchot	3.52	0.35	10	725	5
Shawnee	*3.10	*.33	10	737	5
Little Pine	4.19	.32	14	1,125	13
First Fork Sinnemahoning	3.37	.29	12	792	8
Glendale	2.90	.24	12	519	5
Watershed Soils					
Pinchot	1.01	.09	10	399	0
Shawnee	1.68	.15	14	695	7
Little Pine	1.48	.10	15	310	5
First Fork Sinnemahoning	1.48	.10	14	478	5
Glendale	—	No data available		—	—

TABLE I. -- Continued

Site	Na	K	Ca	Mg	Fe	Mn	Cu	Zn	% Saturation
	Metal Concentrations (me/100g)								
Watershed Soils									
Pinchot - York County	0.3	0.2	4.5	2.0	0.03	0.03	0.01	0.01	52
Shawnee - Bedford	.3	.2	2.2	.2	.05	.06	.01	.01	33
Little Pine - Lycoming	.1	.3	.8	.3	.01	.09	.01	.00+	13
First Fork Sinnemahoning - Potter	.1	.3	.5	.3	.02	.11	.01	.00+	10
Glendale - Cambria		No data available							
Lake Sediments									
Pinchot	.2	.3	6.9	3.5	10.2	2.9	.01	.01	79
Shawnee	.4	.4	6.0	1.4	4.3	3.6	.02	.03	40
Little Pine	.4	.3	5.9	1.0	5.6	2.5	.05	.04	34
First Fork Sinnemahoning	.2	.3	4.4	1.0	2.9	1.7	.03	.02	45
Glendale	.2	.3	3.7	.9	6.3	3.6	.02	.02	71

relationship between heavy metals in the atmosphere and lithosphere and the concentrations found in an estuary.

Contributions of heavy metals from mine spoils, soil erosion, overboard dredging (14), ocean sludge dumping (15), and motor vehicle traffic (16) to rivers and an estuary have been recognized and defined to varying degrees.

Concentrations of eroded soils present in the aquatic environments located within the Delaware Valley also have been quantified (17) (Table I). Heavy metals were extracted with neutral, normal ammonium acetate.

Heavy Metals and Other Pollutants Concentrated by the Marine Biosphere

A number of metals in the water are known to be concentrated by aquatic organisms and plants and in the sediment. Klein (18) found that mercury levels in coastal marine organisms are several orders of magnitude greater than in comparable volumes of sea water. Higher values of mercury are found in sediments near wastewater outfalls as compared to similar deposits further removed. Hellmann (19) gave data for zirconium, copper, zinc, lead, tin, nickel, chromium, manganese, strontium, and rubidium in Rhine River water which included the concentration of dissolved metals. All these metals except tin occurred in the Rhine in concentrations of 0.001-to-1.0 mg/l. Suspended solids in the Rhine River helped remove many of the metals by adsorption.

The amounts of sodium and manganese in shells of small formiminifera and ostracoda (20) indicated that both elements accumulated in close relation with the physiochemical conditions of the basin. Increase in the percentage of sodium content in both types of shells depended on the degree of salinity of the basin. Sodium was less than 0.2 percent in basins of normal salinity, increasing 0.7-to-0.53 percent in basins of elevated salinity, and decreasing in bays diluted by fresh water. High manganese contents were detected in Quinqueloculina akneriana (0.26 percent), cyprideis dutemplei (0.23 percent), and Uirgerina semiornata (0.45 percent) which reflected the effect of the basin depth on the manganese levels in the shells.

Wolfe (21) found that the concentrations of zinc in the Atlantic oyster, Crassostrea virginica were highly variable. Samples from relatively unpolluted estuaries of North Carolina contained an average of 85-to-245 mg/l zinc based on wet weight. Internal tissues, like the abductor muscle and the pericardial sac, contained zinc levels less than half those of the external tissue, but zinc, nonetheless, was distributed uniformly throughout the animal's tissue. Ikuto (22) observed that oysters with abnormally accumulated copper and zinc when transplated into a water area of normal oysters began processes to dispose of abnormally accumulated copper and zine. The accumulation of copper does not start to disappear immediately after transplantation. After 116 days the concentration of copper and zinc feel to values typical of the normal oysters. Dear (23) observed that stable manganese levels in Portugese oysters, which have the ability to concentrate the essential trace element, varys with time.

Lucas (24) measured the concentration of 15 trace metals in samples of whole fish and fish livers from 3 of the Great Lakes. The average concentrations of 7 elements in 19 whole fish from 3 species were 3 mg/l uranium, 6 mg/l thorium, 28 mg/l cobalt, 94 mg/l cadmium, 16 ppb arsenic, 1 mg/l chromium, and 1.3 mg/l copper. An average concentration of 8 elements in 40 liver samples of 10 fish species were 2 ppb uranium, less than or equal to 2 ppb thorium, 40 ppb cobalt, 9 mg/l copper, 30 mg/l zinc, 0.4 mg/l bromine, 30 mg/l arsenic, and 0.4 mg/l cadmium. In most samples other elements observed were 5-to-100 ppb antimony, 2-to-5 ppb gold, 0.5-to-5 ppb uranium, 0.06-to-4 mg/l rubidium, and 0.1-to-2 ppb selenium. Trace element levels varied with species and lake. Uranium and thorium varied with species but not for the same species from different lakes. Levels of copper, cobalt, zinc, and bromine varied little between species and lake, while concentrations of cadmium, arsenic, and chromium varied between species and with species between lakes. Bermarie (25) found that the content of trace elements (manganese, iron, copper, zinc) in muscles and liver of fish from lakes of different geochemical locations depends on the element composition of the environment and the geochemical characteristices of the soil. Bermarie also showed that specific reactions of individual species to the amount of trace elements in the environment show differences in their adaptability. Podsevalov (26) determined the content of potassium, magnesium, calcium, copper, iron, phosphorus, iodine, manganese, and cobalt in 20 species of fish in the Atlantic. Fish muscle tissue from several locations in the Saskatchewan River contained an average of over 1.0 mg/l of mercury. These concentrations were higher than those reported for fish from uncontaminated environments, and corresponded to values reported from Scandinavian fish collected in areas of industrial pollution (Wabeser, 27).

Bermane (28), using emission spectroscopy, determined the levels of iron, manganese, copper, and zinc in muscles, ovaries, liver, gills, kidney, gall bladder, bones, and scales of two freshwater fish <u>Rutilis rutilis</u> and <u>Abramis bramei</u>. Copper was concentrated in the liver and ranged between 23-to-29 and

35-to-40 mg/kg, respectively. Bones contained, respectively, 5.4-to-6.9 and 8.2-to-10.6 mg/kg copper. The highest concentrations of iron were found in the liver (73-to-92 mg/kg), gall bladder (213-to-283 mg/kg), and gills (94-to-127 and 112-to-153 mg/kg). Zinc concentrated in the muscles (18-to-27 mg/kg) and bone (377-to-448 mg/kg). The highest concentration of manganese was in the gills (9 and 13-to-16 mg/kg, respectively), and the scales (12 and 32-to-45 mg/kg, respectively). This study showed the importance of taking either homogeneous samples by homogenizing the fish or knowing what part of the fish was being used to extract the metal.

Martin (29) found that plankton samples collected near the Isthmus of Panama during wet and dry seasons had high levels of iron inshore during the dry season and maximum levels where there was a minimum salinity during the wet season. Zinc and calcium levels increased or decreased in relation to plankton abundance. Distribution of strontium was similar to zinc and calcium in the wet season, but strontium was not detected in areas of strong upwelling currents, in spite of plankton abundance. The manganese levels were high during the dry seasons in areas where either plankton was abundant or tidal scouring marked. In the wet season, manganese concentrations were maximum inshore. Merlini (30) also determined zooplankton and phytoplankton levels in calcium, sodium, potassium, and manganese by activation analysis.

Heavy Metals and Other Trace Metals in the Food Cycle

Water Supplies -- Various trace metals have been measured in water supplies in different parts of the world. Wenger (31) found that drinking water in Switzerland contained approximately 0.4 ug/l molybdenum while the river waters had about 1.0 ug/l and natural mineral waters 0.1-to-50 ug/l. In sheki Zakataly region of Azerbardzhan, Gyul'akhmendev (32) found iodide, cobalt, copper, and manganese levels in water samples to be, respectively, 0.001-to-0.006, 0.002-to-0.01, 0.01, and 0.11-to-0.16 mg/l while the levels in soil at depths of 0-to-30 cm were 0.12-to-0.28 I, 5.8-to-8.0 Co, 9.2-to-13.5 Cu, and 286-to-415 Mn mg/kg air-dried soil; and, in fodder plants, 0.01-to-0.04 I, 0.23-to-1.4 Co, and 2.5-to-14.0 Mn mg/kg plant.

Preobrazhenskaya (33) determined the lead content in rainfall during its natural fallout and during the action of lead iodide on the clouds by emission spectrography. The lead concentration in rain water of natural fallout was approximately one mg/l. Biggs _et al._ (34) found unusually high concentrations of cadmium and to a less extent lead in rainfall and smaller amounts in the streams in Sussex County, Delaware. There was an apparent "residence time" of about 45 days in the unconfined aquifers of the study area.

Animals and Plants -- Because metal concentrations increase in the higher trophic levels and because man is at a high trophic level, the amounts of trace metals in food become important. Mercury content of various food animals has been determined. Westoo (35) found the lowest levels to be 0.003 mg mercury/kg in Danish beef filets compared to pork, reindeer muscle, and liver. Westoo (36) found boiler chicken meat contained 0.005-to-0.009 mg/l. Peden (37) surveyed arsenic, copper, and lead contents of pig and other animal tissue.

Copper and zinc contents of ashed food samples were measured by Osada (38). In marine products examined, the zinc contents were about 0.5-to-3 mg/l with the exception of oysters and crabs which were 50-to-70 mg/l and 16 mg/l, respectively. The contents of copper were 0.1-to-2 mg/l in raw and canned foods, and 2 mg/l in oysters. The copper levels in oysters were high in comparison with other fish.

Barela (39) found that the highest arsenic content in foods of animal origin were in shellfish (0.722 mg/l), while in fish, the dogfish and red mullet contained 0.053 and 0.154 mg/l, respectively. Preserved fish did not vary appreciably in arsenic content. Gargonzola cheese was the highest in arsenic content with 0.124 mg/l, but 0.059 mg/l was found in provolone cheese, while butter contains 0.007 mg/l. Salted meats have 0.019 mg/l, salami 0.020 mg/l, and ham 0.032 mg/l of arsenic. Kifer (40) found selenium levels in fish meals in the range 1.3-to-2.6 mg/l in anchovita, 3.4-to-6.2 mg/l in tuna, 0.49-to-1.23 mg/l in smelt, and 0.75-to-4.20 mg/l in menhaden.

Dobrovol'skii (41) found the coefficient of accumulation, K_b, which is equal to the ratio between concentration of an element in plant ash and the concentration in the soil for a number of elements in plants growing in various geographical areas. K_b was positive for manganese, zinc, molybdenum, copper, nickel, silver, strontium, and barium, but negative for zirconium, titanium, and vanadium. K_b was found to be approximately equal to one for cobalt, gallium, cerium, yttrium, and beryllium. Therefore, the amount of various metals in food depends on the characteristics of the soil on which it is grown.

Man --Trace metals have been detected in man. Because of man's position at the higher trophic level in the food chain, the concentration of metals within the body becomes an important health consideration. Healthy subjects contained 0.29 ug/100 ml of nickel in serum, 0.48 ug/100 ml in whole blood, and 0.23 ug/100 ml (2.4 ug/day) in urine. Patients 24-hours after a mycardial infarction have a mean nickel level of 0.51 ug/100 ml [Nomoto (42)]. Molokhia (43) (44) determined zinc and manganese levels in normal skin.

Cadmium loading of humans from food and drink was determined by Essing (45) and Rautu (46) to be 48 ug/day as a mean oral cadmium load, with concentration range of 38-to-64 ug/day. Rautu (46) estimated that grain and grain products supply 42-to-56 percent, meat and meat products 21-to-29 percent, and vegetables 8.5-to-11.2 percent.

Poggini (47) found the mean values for calcium, magnesium, iron, copper, and zinc in normal children's blood between 3-and-14 years of age to be 9.45± 0.30 mg/1, 1.52± 0.8 milliequivalents/1, 11 ± 11 mg/1, 124 ± 8 mg/1, and 120 ± 13 mg/1, respectively. In normal men and women, the mean value for magnesium in plasma was 2.16 mg/100 ml; for magnesium in human muscle, 93 mg/100 g dry muscle Hunt (48) . In normal babies, meconium concentrations of iron, copper, and zinc were 89, 56, and 290 ug/g, respectively, but, in the premature child and in the light-weight child at birth, iron and copper levels were high [Tanaka (49)]. Dubinskaya (50) found the contents of copper, zinc, and manganese (ug/g dry weight) to be 10-to-13, 220-to-298, and 29-to-56, respectively, in human hair.

Minimato is a disease that was first noticed in the late 1960's in Japan. It has been established that the mercury level in the body and this health disorder are related. Persons with Minimato had a diet which included fish contaminated with mercury [Reickenback-Klinke (51)]. Bergeund (52) calculated from a linear relationship of intake and erythrocyte levels of mercury among fish-eating individuals in Sweden the human body burden of methyl mercury. The ease with which other organo-metallic compounds are assimilated in the human food chain has been noted. The body of literature which substantiates this concern is growing rapidly. However, the analytical techniques used to distinguish between organo-metallic compounds and other species are still in a developmental stage in terms of sensitivity and reliability.

Previous Delaware River - Bay Studies

A portion of the first-year objective will be an evaluation of existing information. Previous Delaware River-Bay studies are listed in Appendix II.

Conclusions

The presence of trace contaminants such as heavy metals in the food chain is the result of complex reactions, inputs and outputs of these pollutants within the system. Through a careful literature search and by examining the concentrations of metals in an orderly and statistically meaningful manner, these trace contaminants can serve to demonstrate the food chain relationship within the system.

IV PROPOSED PROGRAM

IV. Proposed Program

Objective

This multi-disciplinary approach will develop the methodology for an estuarine-zone warning system using heavy metals for the demonstration. Statistical and predictive modeling will be based on historical information and a rigorously designed experiment. Sample preparation and analysis during the test will be based on on-going research by the Department of Natural Resources and Environmental Control. Implementation of study results will be a continuous function designed to take advantage of relationships determined during the study.

Evaluation of Background Information

The Department's Environmental Control Laboratory has been evaluating, on a continuous basis, methods for the analysis of heavy metals in air, water, soil, benthic, shellfish, and invertebrate samples. The Division of Fish and Wildlife has been sampling the oysters and other estuarine fauna by various methods for trace metal analyses for the past two years. Air and water samples have been tested successfully using an atomic absorption spectroscopic analysis on concentrated samples. Although AAS methods also are used for shellfish, invertebrate, and benthic samples, the methods of sample preparation are considerably more involved.

Sampling Design

The statistical format used for this study was selected for its flexibility, i.e., its capacity for alteration as new information becomes available. This approach will yield not only present pollution levels within the estuarine system, but also will provide relationships between parameters which will permit a less extensive sampling network.

The objectives of the analysis are:

1. To determine quantities of heavy metals from input and output determinations.

2. To establish existing levels of heavy metals in the atmosphere, water, soil, benthos, and indicator organisms, as well as other chemical, physical, and biological factors.

3. To find the correlation between levels of heavy metals in the environment and indicator organisms and biological factors.

4. To evaluate indicator organisms as representative of sampling locations in the estuary.

The sampling plan has been formulated with the specific objectives of statistical estimation and correlation development. The plan is limited mainly by the number of sites that can be sampled within the specified time period.

For purposes of the analysis, a sufficient number of data points will be selected to establish correlation at each sampling station with a statistical significance at 95-percent confidence level. Variables showing the highest degrees of correlation will be considered as "first selection" parameters of the system. Sampling frequency for these parameters will be dependent on periods of maximum oyster activity. Because of the large number of samples (minimum of 60) that must be processed within the approximately one-year sampling period, samples at each station will be taken at different tidal times. Tidal as well as temporal and spatial variations in concentrations will be evaluated for water samples. Special attention will be paid to axial variations within the estuary with the idea that some or all of the constituents studied may be characterized consistently by fewer sampling points. Data input into the preliminary model will be continuous so that changes and corrections to sampling locations, frequency of sampling, sample time, etc., can be implemented with a minimum of wasted time.

To determine the avenues of entrance for heavy metals into the food web, atmospheric, soil, water column, benthic, and indicator organism sources will be investigated (Table I).

TABLE II. -- First-Year Sampling Design*

System	Location	Parameter	Frequency±	Method
Air				
	Dover AFB+ Wilmington Airport Cape May Maurice River Milford	Particulate- Heavy Metals	May-Nov., twice weekly; Dec.-April, monthly	AAS analysis of solvent extracted high-volume pump samples
	Lewes			AAS analysis of rainfall
Rainfall	Same as for Air	Heavy Metals	As needed	
Water Col.				
four ft depth	1 - 15	Salinity	"	Probe
		Chlorosity	"	Probe
		Heavy Metals	"	AAS analysis of water samples
		BOD	Monthly	Std. Methods
		DO	"	"
		Nitrogen	"	"
		Phosphorus	"	"
		Phytoplankton	"	"
		Zooplankton	"	"
		Total Carbon	"	TC analyzer
		Turbidity	"	Std. Methods
		Alkalinity	Quarterly	"
		Acidity	"	"
		Fecal Coli.	"	"
		Fecal Strep.	"	"
		pH	"	"
		Total coli.	"	"
bottom depth	1 - 5	Same as above		
Benthos	1 - 15	Heavy Metals	May-Nov., twice weekly; Dec.-April, monthly	AAS analysis of reduced sample
		Total carbon	"	TC analyzer

*Second-year sampling design for the atmosphere, water column, benthos, and oyster analysis will be dependent on relationships established with first-year study.

+Bombay Hook may be substituted in place of the airport site.

±First choice parameters will be sampled twice weekly; second choice, monthly; and, third choice, quarterly.

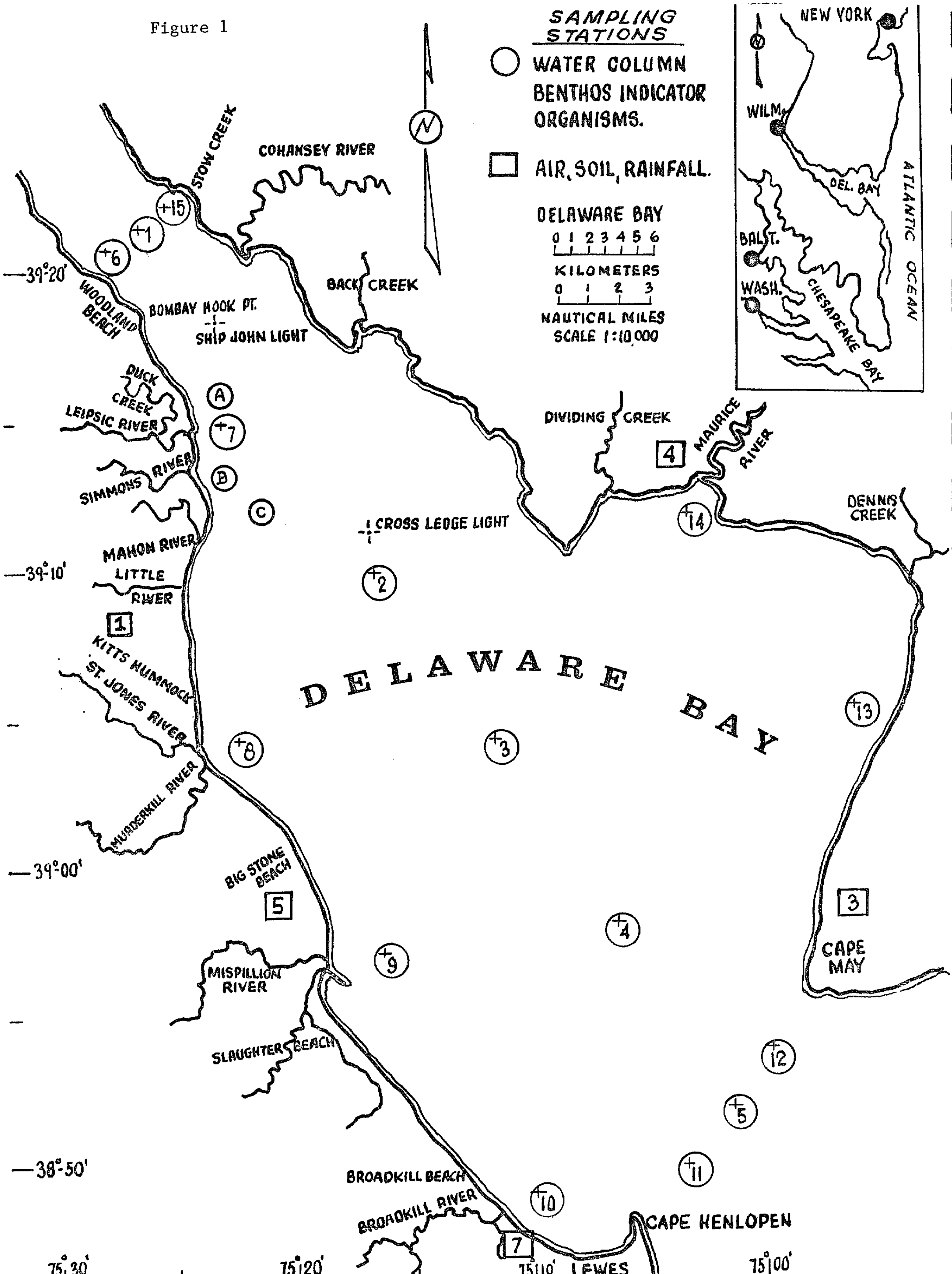
Sampling Locations

A total of 15 sampling locations within the estuary was selected for study. This number of sampling sites, shown in Figure 1, will provide representative concentration profiles for water column, benthic, and indicator organism data. In addition, three natural oyster beds will be sampled on a regular basis.

Six air, rainfall, and soil monitoring stations also were selected (Table III).

During the first year of this study, an evaluation of each station will be made. If it is found that certain stations can be omitted without affecting project goals, such modifications will be made.

Figure 1



SAMPLING STATIONS
WATER COLUMN BENTHOS INDICATOR ORGANISMS.
AIR, SOIL, RAINFALL.
DELAWARE BAY
0 1 2 3 4 5 6
KILOMETERS
0 1 2 3
NAUTICAL MILES
SCALE 1:10,000
NEW YORK
WILM.
DEL. BAY
ATLANTIC OCEAN
BALT.
WASH.
CHESAPEAKE BAY
STOW CREEK
COHANSEY RIVER
BACK CREEK
WOODLAND BEACH
BOMBAY HOOK PT.
SHIP JOHN LIGHT
DUCK CREEK
LEIPSIC RIVER
SIMMONS RIVER
DIVIDING CREEK
MAURICE RIVER
DENNIS CREEK
CROSS LEDGE LIGHT
MAHON RIVER
LITTLE RIVER
KITTS HUMMOCK
ST. JONES RIVER
MURDERKILL RIVER
DELAWARE BAY
BIG STONE BEACH
MISPILLION RIVER
SLAUGHTER BEACH
CAPE MAY
BROADKILL BEACH
BROADKILL RIVER
CAPE HENLOPEN
LEWES
39°20'
39°10'
39°00'
38°50'
75°30'
75°20'
75°10'
75°00'

TABLE III. -- Placement of Water and Air-Sampling Stations

Station Number	Location
Water Sampling	
1, 6, 15	Head of Delaware Bay
2	Axis of channel
3	"
4	"
5, 11, 12	Mouth of Delaware Bay
7	Leipsic River (off shore)
8	St. Jones River "
9	Mispillion River "
10	Broadkill River "
13	Between Cape May and Dennis Creek
14	Maurice River (off shore)
Air Sampling	
1a	Dover Air Force Base
2a	Wilmington Airport or Bombay Hook
3a	Cape May
4a	Maurice River
5a	Milford
6a	Lewes

Table III. -- (Continued)

Station Number	Location
Rainfall Sampling	
1r	Dover Air Force Base
2r	Wilmington Airport or Bombay Hook
3r	Cape May
4r	Maurice River
5r	Milford
6r	Lewes
Soil Sampling	
1s	Approximately the same as for Air Sampling
2s	
3s	
4s	
5s	
6s	

Statistical Analysis

Factor analysis will be carried out on variables such as heavy metal concentrations and the biological and chemical considerations. The objective will be to try to establish whether or not the many variables in the system can be explained by fewer factors. Such factors may generally be described as (a) environmental, (b) biological, (c) chemical, and (d) food chain. The analysis will also provide an indication of (a) the relationship between changes in the levels of heavy metals to other environmental considerations, (b) the relationship between heavy metals in existing oyster populations to that in "tray" oysters, and (c) the relationship of heavy metal concentrations in the environment to metals in the human food chain (oysters).

Analysis of variance will be carried out to establish the levels of heavy metals at each station and to seek the differences in concentration levels. The analysis will provide statistical tests for station differences, time differences, and spatial-by-temporal interactions. If any of these tests are found to be significant, a surface will be generated (a model) to characterize the level of the heavy metals over the study area.

The data yield for first- and second-choice parameters (Table II) is shown in Tables IV and V, respectively.

TABLE IV. -- Data Yield for "First-Choice" Parameters*

Required for 95-Percent Confidence in Correlation Coefficients

System	Number of Samples/Year	
	Heavy Metals	Others
Air	2,520+	--
Rainfall	+	
Soil	168	
Water Column		
four-ft	6,300	1,800
bottom	6,300	1,800
Benthos	6,300	900
Oysters	7,560	--
	29,148	4,400

*It is assumed that 7 heavy metals will be analyzed at 15 estuary locations and 6 air sampling sites. During the preliminary sampling and testing, only axial sampling locations (5) will be studied, thus reducing "First-Choice" data to less than 10,000 pieces.

+Does not include rainfall or soil analyses.

TABLE V. -- Data Yield for "Second-Choice" Parameters

System	Number of Samples/Year	
	Standard Methods	Others
Atmosphere	--	--
Water Column		
four-ft	1,980	180
bottom	1,980	180
Benthos	120	--
Oysters	--	--
	4,080	360

Mathematical Model Development

General Considerations: The basic approach to be employed in the first year of the proposed study considers data collection and statistical analysis of the observations as the major activities. The first year's effort will also include modest efforts at data analysis employing mathematical models. It is intended to examine the observed data employing a summer and winter seasonal steady-state compartment modeling framework with linear kinetic assumptions and up to 15 spatial compartments.

The modeling efforts proposed for the first year are to be viewed as a test of the feasibility and utility of modeling the flow of heavy metals in the system. Feasibility will be examined in terms of engineering and scientific considerations and in terms of the usefulness of model output for decision making and/or system management and control. The results of the modeling efforts in the first year's program will be employed to develop recommendations for the subsequent effort. Recommendations would include an assessment of the utility and desirability for additional modeling, and any required modifications in the data collection program.

Proposed Modeling Effort: The notion of compartment as used in this proposal is defined as any water resource or ecological variable, suitably located in space. This definition of compartment arises, on the one hand, from the finite difference approximation of partial differential mass balance equations. Continuous space is replaced by discrete finite elements or spatial compartments within which are located (usually uniformly distributed) the variable of interest. On the other hand, concepts from quantitative ecological models are also employed; where the "continuum" of the environment is replaced by finite, discrete, interacting trophic levels. It is therefore possible to consider modeling variables in the spatial domain (such as the concentration of a metal in the water column or benthos) and variables in the state domain (such as the concentration of metals in the oyster or plankton biomass). Physical volume and mass in the spatial domain corresponds to biomass in the state domain. In addition, residence time in the spatial domain corresponds to mean ages in the state domain.

1. Mathematical Structure

With the general notion of a compartment in mind, one can define C_{ir} as the i^{th} variable located in the r^{th} spatial position. Interactions between variables can be considered as linkages; such linkages including, for example, physical transport of a variable from location r to location s. Alternately, one can consider causal linkages which transform variable i to variable j. It is proposed to employ linear kinetic assumptions for all causal linkages.

This assumption is made for two basic reasons. First, it is difficult, if not impossible, to specify in great non-linear detail, all the complex mechanisms that may exist in this problem context. Further, it is not necessarily clear that such a detailed specification is any better than a broad linear interactive system. Finally, the mathematical and computational aspects of solving systems of interactive linear equations are well understood.

For the year one study, a steady state approximatation is to be made to aid in determining the order of the kinetic interaction coefficients.

In general, one can consider a link as $K_{ij,r}$, which represents the causal transformation of variable i to variable j at location r. It is convenient to distinguish further the mass transport links as $F_{i,rs}$, which represents the bulk transport of variable i from location r to location s. With this notation, Equation (1) can be written:

$$0 = \pm \sum_{s=1}^{n} F_{i,rs}C_{is} \pm \sum_{j=1}^{m} K_{ij,r}C_{jr} + g_{i,r} \qquad (1)$$

where $g_{i,r}$ represents an input forcing function of variable i at location r. This expression represents a discrete version of a mass balance around the i^{th} compartment, and is composed of transport over all spatial compartments bordering on r, plus the causal transformation of all j variables linked to i, all located at the r^{th} position.

The resulting vector equation can be written as:

$$[\overline{K}]\ (\overline{C}) = (\overline{g}) \qquad (2)$$

where $[\overline{K}]$ is an mn x mn matrix of interactions, $(\overline{C})$ is an nm x 1 vector arranged in such a way that the first n elements represent the distribution of c_{ir} (r = 1 . . . n), the second set of n elements represents the distribution of C_{2r} (4 = 1 . . . n) and so on. The vector $(\overline{g})$ is interpreted similarly for the input forcing functions.

This set of equations can be viewed as representing an equilibrium situation. In this case, it is necessary to have all elements of $(\overline{C})$ positive for physically realistic results. That is, the problem would lose its meaning if after solution of $(\overline{C})$, it was discovered that the metals concentration in the phytoplankton compartment became negative. It can then be shown that all terms off the main diagonal of $[\overline{K}]$ must be negative for an all-positive vector $(\overline{C})$. The major ecological consequence of this restriction is that direct inclusion of predation or other similar effects <u>is not possible</u>.

2. Year One Efforts

Two heavy metals of the seven to be measured in the data collection program will be modeled in year one. The metals selected will not have similiar kinetic properties, thus two associated metals will not be considered in year one.

The specific modeling variables to be considered in the first year's modeling effort are:

(a) the metal concentration in the water column (mg/l),

(b) the metal concentration in the benthos (mg/gm),

(c) the metal concentration of the plankton (mg/gm biomass),

(d) the metal concentration in air samples (ug/m^3),

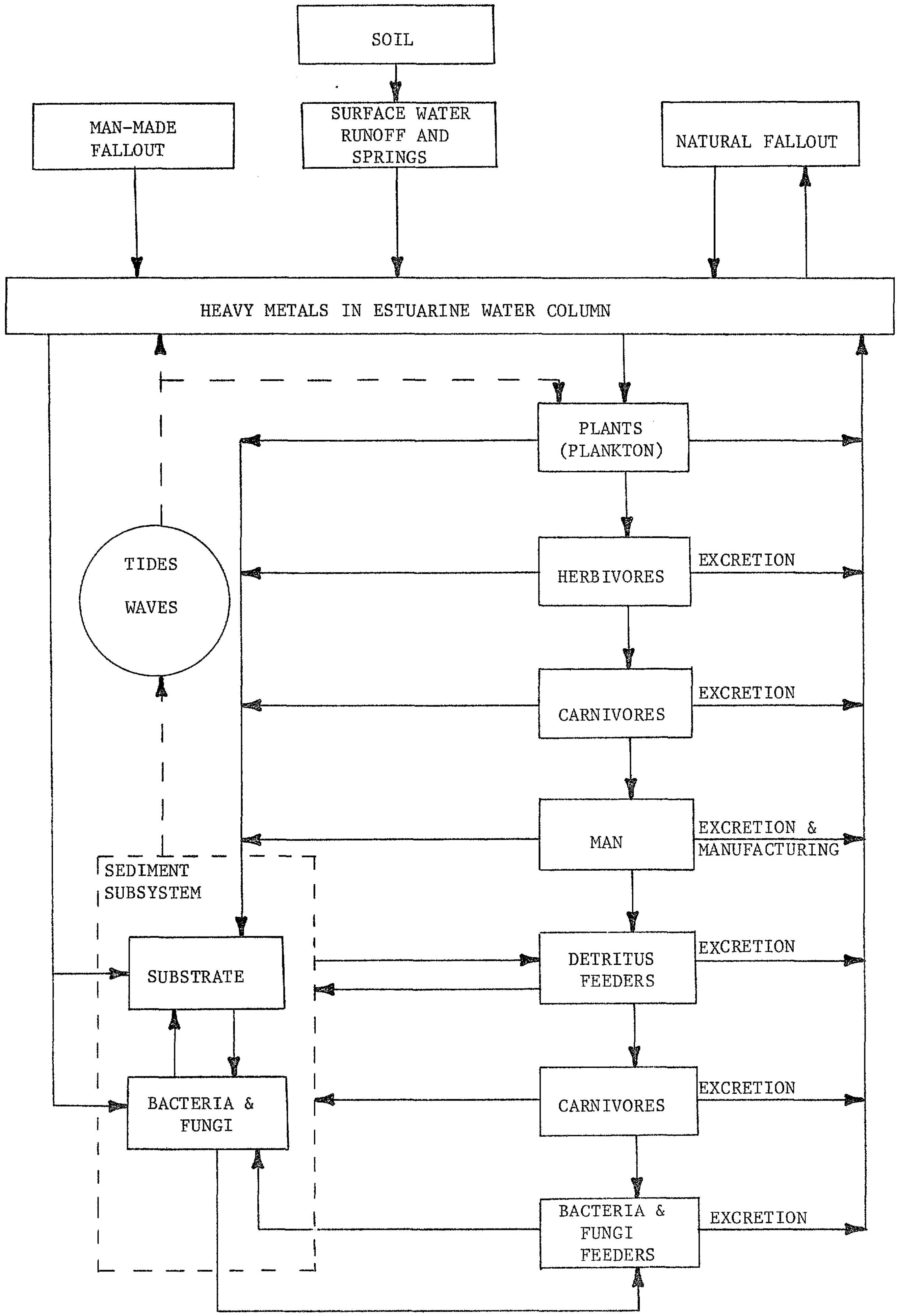
(e) the metal concentration in soil samples (mg/gm),

(f) the metal concentrations of the fishery (mg/gm biomass), and

(g) the metal concentrations of oysters (mg/gm biomass).

It will be noted that the modeling effort uses broad compartment variables for the major portions of the system and then narrows the area

FIGURE 2



Adopted from Odum, E.P., 1971, Fundamentals of Ecology, W.B. Saunders Co., Phila., Pa. 19105 of concern in the last system variable, the oyster. One of the overall project objectives is to examine the possible use of the oyster as a reliable indicator of contamination of the general environment and, in particular, the possible contamination of a valuable and desirable human food source.

Modeling of these variables will be carried out on a summer and winter seasonal steady-state basis and will include the evaluation of the system hydrodynamics, volume, mass and biomass. It is anticipated that a maximum of 15 spatial segments will be considered in the year one modeling effort to cioncide with the observed data locations. The modeling effort will use as input, data collected on sources of heavy metals from the terrestial areas (such as industries, municipal sources, agricultural and undeveloped lands) while also considering the atmospheric input to the marine environment. Thus the system is composed of a wide range of sources of contamination and system variables as shown in Figure 2. Significant elements of the system will be considered.

A portion of the first year's effort related to the modeling process will be the collection and utilization of existing historical data on flow patterns, mixing, metal transfer rates and concentration factors at various trophic levels. These data will be analyzed and used in conjunction with the specific information collected as part of the proposed study in the first year's modeling effort.

The proposed modeling effort will allow comparison of observed and calculated results under four different conditions (winter and summer for two metals). Evaluation of the results of these efforts will then be carried out to develop recommendations on the utility of modeling in system management and control. Further, the results will be examined to determine the most appropriate modeling framework and structure (time variable, non-linear kinetics, et al.) to facilitate analysis of system behavior, management and control alternatives. An example of the types of considerations which will be examined is the possible year-to-year carryover to metals at the various levels and the impact of this phenomena on concentration factors. If year-to-year carryover is significant, then it will be necessary to have non-steady state modeling in subsequent year's modeling work. Finally, the modeling effort will provide one of several bases for review of data collection programs in subsequent years of the study.

A section of the project report will be prepared which represents the results of the first year's modeling efforts and analysis. Recommendations on the extent and framework for future modeling efforts and data collection programs will be included in the report section.

It is anticipated that the modeling efforts in the second and third years of the project will examine the remaining significant non-associated metals and will include as necessary and appropriate, additional spatial detail, time variable, or non-linear kinetic links identified in the year one study.

Sample Preparation

Preparation of Biological Samples -- Biological samples must be solubilized prior to metal analysis. Methods routinely used are acid digestion, wet oxidation, dry ashing, and lyophilization.

Acid digestion involves heating samples with an acid or a combination of acids until the material is completely solubilized. Acid mixtures such as nitric acid - perchloric acid - sulfuric acid [Savoy (53)] or sulfuric acid - nitric acid [Hasogaki (54)] commonly are used as well as single acid digestion. It is a rapid method and compares well with ashing and acid oxidation digestion [Premi (55)] .

Wet oxidation destroys organic materials thus freeing organically combined elements. Digestion by incubation with sulfuric acid - chloric acid or sulfuric acid-nitric acid is the first step. The addition of nitric acid prevents darkening of the sample solution, making it easy to see when the sample has been solubilized completely. [Armstrong (56)]. The digested material then is oxidized with potassium permangante, cleared with hydrogen peroxide, and reduced with naphthylamine hydrochloride [Naito (57)].

In dry ashing, the sample first is dried and then ashed in a muffle furnace at approximately 500°C. The ash then is dissolved in acid [Corbi (58)] [Gotsulyak (59)] [Osada (60)] [Srivastava (61)] [Maksimov (62)]. Volatilization of some trace elements such as zinc and cesium is a disadvantage of dry ashing [Tusi (63)] [Blume (64)].

Wet ashing does not require drying of samples prior to heating. Hydroxide radicals from H_2O_2/Fe^{+2} (Fenton-Reagent) in aqueous solution is practical for large numbers of samples per run. Mild conditions and low losses of trace metals are advantages of this method [Sansoni (65)]. Ashing by heating materials in a 450°C muffle furnace is another wet combustion method [Gotsulyak (59)].

Freeze drying or lyophilization followed by acid digestion is another method of sample preparation [Shuster (66)].

Preparation of Benthic Samples -- Soil and sediment samples can be digested rapidly and easily with acids such as hydrochloric, hydrogen fluoride-sulfuric acid mixtures, or aqua regia [Novikov (67)] [Panin (68)] [Frank (69)]. In a more complicated procedure, the sample is heated to a high temperature with nitric acid and hydrogen fluoride in a platinum crucible and then dissolved in acid [Mineeva (70)]. Trace elements may be determined directly by atomic absorption methods or colorimetric methods, or they may be concentrated prior to analysis. Extractions may be made with EDTA [Ure (71)], with dithizone [Kabanova (72)], or with organic solvents [Wenger (31)].

Sample Analysis

In the past 10 years, atomic absorption spectrophotometry has been accepted widely for analysis of heavy metals in a variety of samples. Rapid and sensitive methods give an advantage to this technique where large numbers of analyses are required. The technique generally is limited to metals in solution, although methods have been reported for the analysis of solids.

Samples require a minimum of preparation for direct analysis. Water samples either can be analyzed directly or following the addition of acid to solubilize suspended matter [Stephan (73)] [Taras (74)]. Biological materials require digestion prior to analysis. Acid digestion, ashing, and wet oxidation techniques are used the most commonly for sample preparation. After pretreatment, samples may require concentration to determine the presence of trace elements.

Minute concentrations of trace metals can be determined after chelation, followed by organic extraction. Metal enhancement of from 2 to 10 times by use of complexing agents and solvent extraction have been found [Chakrubaiti (75)] [Kuwata (76)].

Esters or ketones are suitable solvents for extraction because they burn completely and provide a stable flame. Methyl isobutyl ketone frequently is used because it is relatively insoluble in water and gives high and stable absorbance [Kuwata (76)]. Other commonly used solvents are chloroform, methylalcohol, tert-butyl alcohol, and dioxane. Lower detection limits are directly proportional to organic solvent concentration and inversely proportional to metal concentration Delibas (77) .

Chelating compounds frequently used are ammonium pyrrolidine ditheoeoiliomate (APDC), sodium diethyldithiocarbomate (Na-DDTC), dimethyl glyoxime, and 8-hydroxyglyoxime.

One suitable method for concentrating metals in water samples involves the use of APDC and MIBK. It is a rapid and practical method for analyzing a large number of samples [DeFilipo (78)].

The use of sampling boats with a heated graphite tube can improve atomic absorption sensitivity 10 to 100 times. Small volumes of sample are required and levels of metals can be determined without preconcentration or extraction [Paus (79)] [Fernandez (80)] [Manning (81)].

It is also possible to produce a vapor of metal atoms by means other than a flame. For example, mercury may be measured by passing mercury vapor through a quartz cell in the path of a hollow cathode mercury lamp and measuring absorption at the characteristic wavelength [Chau (82)] [Kalb (83)] [Armstrong (52)]. This method can detect as little as 0.5 mg/1 mercury.

Atomic absorption and flame emission are closely related, and many instruments have the capability of both techniques. For most analytical purposes, atomic absorption has shown itself to be superior. Interaction between metals in the analysis of natural waters is a disadvantage of emission spectrometry. However, alkali metals and a few other easily excited atoms can be detected and measured to lower concentrations by flame emission. For qualitative scanning of samples, emission spectrometry is advantageous, but for quantitative analysis, atomic absorption is the more satisfactory.

Implementation of Study Results

This research program is aimed at developing the methodology for the establishment of an estuarine zone ecological warning system. The methodology thus developed ultimately will define quantitatively the impact of any waste discharge on the system. This project will establish statistical and analytical guidelines thus providing a first step in relating water, air, soil, and benthic quality with the human food chain.

Additional studies covering pesticides, radio-nuclides, chlorinated hydrocarbons, etc., and their interaction with the environment and the human food chain will be a natural outcome of this initial thrust involving heavy metals.

Supervisory Functions and Project Reporting Lines

Messrs. Otto and Lesser in this team effort share the responsibility in all critical research program decisions. Such areas as program design, selection of analytical methods, project timetable, experimental approaches and project coordination are included. The principal investigators will be responsive to a Technical Advisory Group composed of Department Personnel. Other supporting services described elsewhere in the proposal will be drawn into the program as required.

A chart showing the supervisory functions and reporting lines follows (Figure 3).

Project Schedule and Milestones

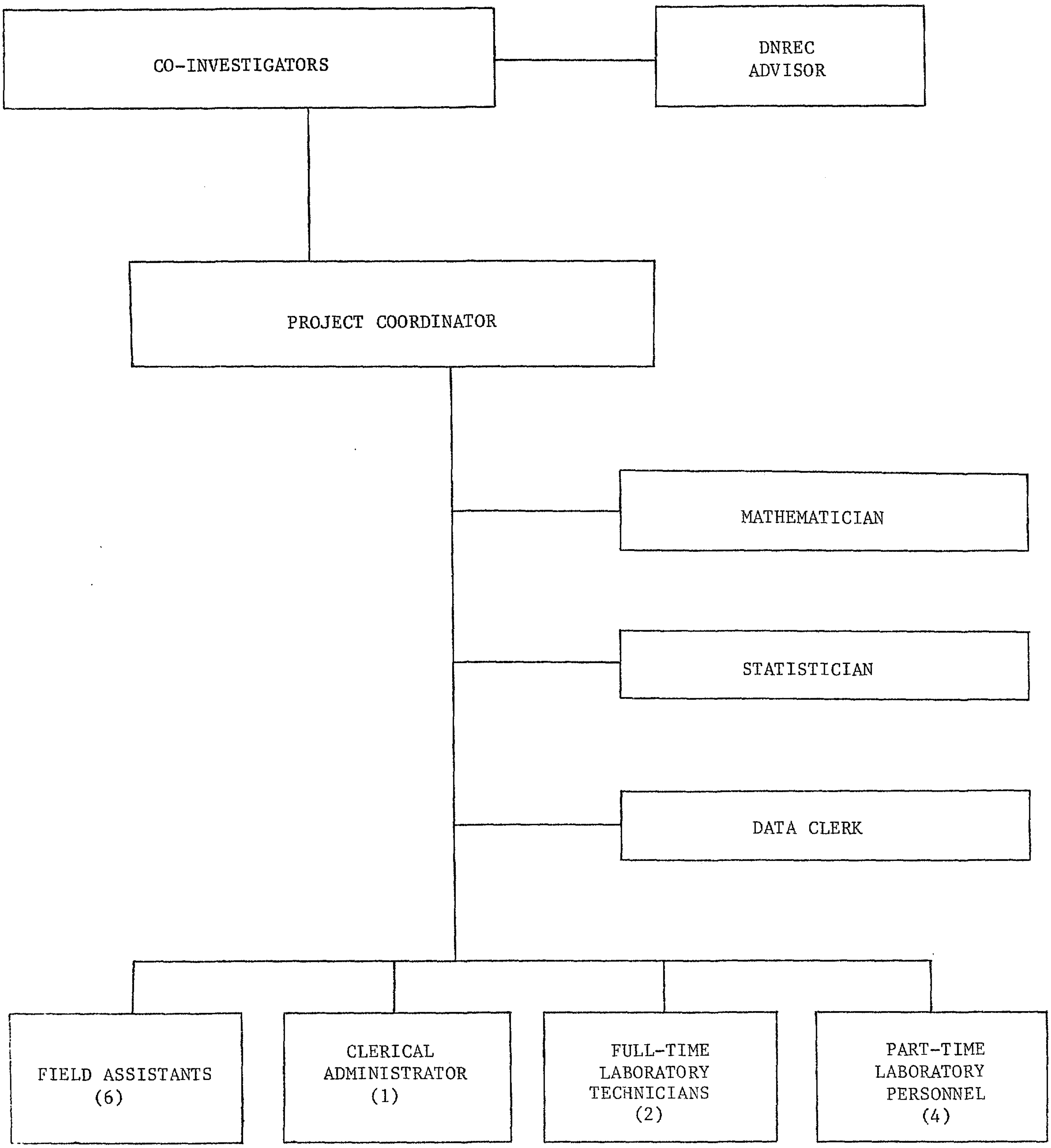
A chart indicating the time-phasing of the key elements in this project are shown in Figure 4. The time scale shown is approximate.

There will be several distinct phases in the project development, which are indicated. It should be noted that there is a definite overlapping of various elements in the project, and that during the three year giant duration of the project, the primary emphasis will shift from development to demonstration and verification of the model.

Model Utilization

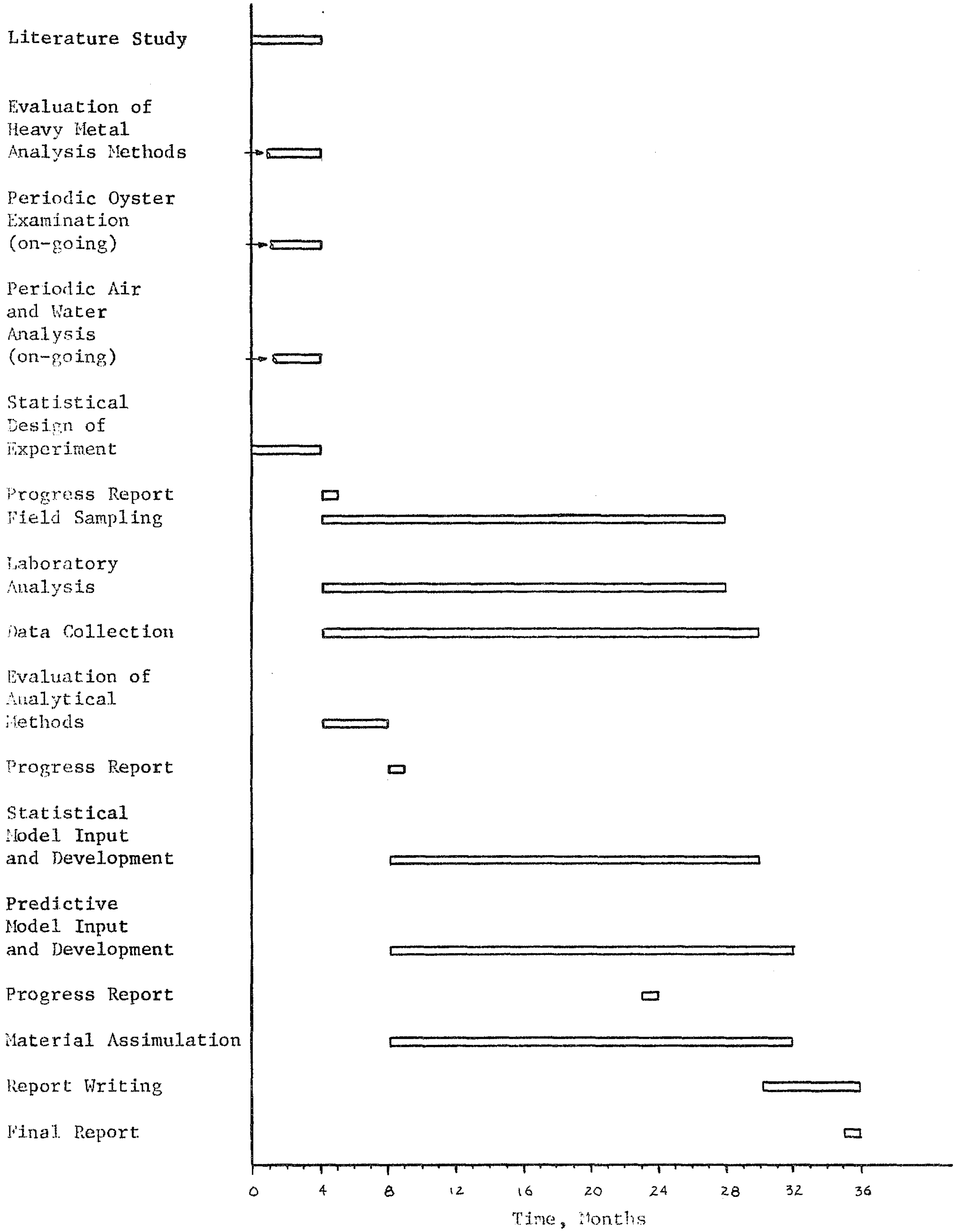
Model development and the steps to achieve this development are the objectives of this program and will provide the basis for the estuarine zone ecological warning system. The system will permit not only identification but interpretation of abrupt changes and more subtle trends within the system.

FIGURE 3



CO-INVESTIGATORS
DNREC ADVISOR
PROJECT COORDINATOR
MATHEMATICIAN
STATISTICIAN
DATA CLERK
FIELD ASSISTANTS (6)
CLERICAL ADMINISTRATOR (1)
FULL-TIME LABORATORY TECHNICIANS (2)
PART-TIME LABORATORY PERSONNEL (4)

FIGURE 4



PROJECT SCHEDULE

This information can be shared with local and federal agencies for the purpose of problem identification and abatement action. Also, data thus collected and analyzed will be made available to other researchers. In like manner, findings by others affecting model limits, parameters, etc., will be incorporated in the Delaware system. Thus, the mechanism will be established whereby continuing input and output information will be utilized for the further improvement and tuning of the system.

V BUDGET

V. Budget

Budget for First Year

The budget presented is based on the satisfaction of program objectives using a multidisciplined approach within the Department. Should it be deemed advantageous for the Department to act solely as administrator for this project, with equipment and expertise supplied primarily by outside (university, institute, etc.) sources, an estimated 100% "overhead" cost will need to be added to the following budget.

Salaries and Wages	Percent Time	Cost
1-Principal Field Investigator	25	$ 5,000
1-Principal Lab Investigator	25	5,000
1-Project Coordinator	100	15,000
6-Field Assistants	100	48,000
2-Laboratory Technicians	100	16,000
1-Clerical Administrator	100	7,000
1-Data Clerk		5,000
2-Graduate Students	1/2	6,400
		$ 107,400

Permanent Equipment	Cost
Biological Sampling Gear	5,000
Scuba Equipment, Hydraulic Lifts, Etc.	20,000
Laboratory Analytical Equipment	20,000
Research Vessel for Sampling	100,000
	$ 145,000

Contractual Services	Cost
1-Statistician for data analysis	2,000
1-Mathematical Model Development (See Below)	40,000
Computer Time	2,000
	$ 44,000
Expendable Supplies and Materials	
Trays, Ropes, Buoys, etc.	3,000
Laboratory Supplies	20,000
	$ 23,000
Travel	
Vehicle Rental	4,500
Scientific Meetings	750
Equipment Rental	
1-Boat for Sampling, $250/day, 60 days	15,000
Preparation and Publication of Data	3,000
First-Year Cost:	$ 342,650

Summary - Budget First Year (Inhouse or Administrated)

Inhouse Project - Department of Natural Resources and Environmental Control (DNREC)

DNREC	$302,650
Contractual (Mathematical Model)	40,000
Total:	$342,650

Administrated Project - DNREC Coordinates Contracts with University, Institutes, etc.

DNREC	$ 90,795
Contractual (Mathematical Model)	40,000
Contracts	514,505
	$645,300

Mathematical Model Development Budget

The estimated costs for the first year's modeling efforts are:

Task 1 - Model Setup and Historical Data Analysis:

(a) minor modifications of existing programs for Delaware Bay modeling effort,

(b) collect and analyze data on:

(1) Hydrodynamic regime
(2) System mass and biomass
    (i) oyster
    (ii) fishery
    (iii) plankton
    (iv) bottom accumulations

(3) Metals concentration factors and kinetic transfer rates
(4) System geometry
(5) System inputs

Manpower Cost	$ 8,000

Task 2 - Modeling Effort

(a) Make modeling runs for two metals - summer and winter conditions,

(b) analysis and evaluation of modeling results and comparison to observed data,

(c) evaluation of modeling effort in terms of its utility to system management and control, and

(d) development or program for subsequent years of the study

(1) Model framework (if any)
(2) Revision of data collection programs (if any).

Manpower Cost	$19,000

Task 3 - Meeting, Project Coordination Report Preparation

Manpower Cost	$ 6,000

Expenses

Computer	$ 5,600
Expenses	$ 1,400
Total Project Cost:	$40,000

Budget for Second and Third Years

Second and third-year costs for this project are estimated as follows:

Budget for Second Year

Salaries and Wages - \$107,400 + \$107,400 x 5.0% =	\$ 112,770
Contractual Services (Statistician and Computer Time)=	4,000
Expendable Supplies and Materials	10,000
Travel	3,000
Second-Year Cost:	\$ 129,770

Estimated Budget for Third-Year

Salaries and Wages - \$112,770 + \$112,770 x 5% =	\$ 118,409
Contractual Services (Statistician and Computer Time)=	4,000
Expendable Supplies and Materials	10,000
Travel	3,000
Total Third-Year Cost:	\$ 135,409

VI UNIQUE QUALIFICATIONS & FACILITIES

VI. Unique Qualification and Facilities

The Delaware Department of Natural Resources and Environmental Control has participated in numerous cooperative research programs including the following:

Cooperating Agency	Study Area
Delaware River and Bay Commission	Delaware Bay
University of Delaware	Delaware Bay
Board of Health	Interstate Water Quality
Medical Examiner	Laboratory Analyses
Department of Agriculture	Food Processing; Irrigation
Delaware USGS	Nitrate Surveys
Chesapeake Technical Support Lab	Estuary Surveys
New Jersey Department of Environmental Protection	Delaware Bay
Federal EPA	Air and Water Pollution Studies
Federal EPA	Solid Waste Demonstration Resource Recycle Plant

The comprehensive air and water resource program established by the Department has resulted in a first-class monitoring effort by the Division since 1969 to measure continuously sulfur dioxide, particulates, oxides of nitrogen, hydrocarbons, carbon monoxide, ozone, and total oxidants.

The water resources program also has been ambitious. The program of pollution surveillance of over 350 sampling sites, interstate streams and wastewater treatment plant discharges continues on a monthly basis providing a data base of over ten years. Over 5,000 water quality samples are collected and analyzed each year, thus providing vital information on the quality of the waters within the State and adjacent coastal waterways.

The Department's Environmental Control Laboratory is one of the leading governmental research laboratories in the United States and is highly experienced in performing routine tests, e.g., "Standard Method" techniques (74), as well as the more sophisticated tests. Laboratoty capabilities, in addition to "standard" testing facilities, include atomic absorption, gas chromatography, wet-chemistry auto-analysis (all three pieces of equipment have full-time operators), plus carbon analyzers, spectroscopy, and other research tools. Supplementing the 11 full-time laboratory personnel is a five-man sampling team with equipment support (one ocean-vessel suitable for all weather Bay sampling) and experience (this group was the nucleous of the recent two-year Bay study funded by the Delaware River and Bay Commission) suitable for the needs of this project.

The Division of Fish and Wildlife is responsible for the management of shellfishes and finfishes in all waters under the jurisdiction of the State. A six-member team of fishery biologists are presently conducting basic and applied research with cooperation from the University of Delaware on various species of fish in the Delaware estuary.

The Management Program administered by the Division of Fish and Wildlife for the Delaware estuary is presently undergoing revisions and indepth research. The return of a disease resistant oyster after the catastrophic parasitic protozoayn MSX in the mid-fifties will enable the return of a $5,000,000/year seafood industry. All oyster beds are being mapped and $50,000 is being expended to expand the natural oyster beds to their historic boundaries. Research on the oyster as to its heavy metals content is being conducted on a monthly basis throughout the Delaware Bay.

These studies are supported through the Sea Grant Program administered by the University of Delaware.

The Hard Clam population of the Delaware Bay is being determined by cooperative efforts with the University of Delaware and supported by the National Marine Fisheries Service (NMFS). NMFS also supports the monitoring of oysters for productivity, growth and survival.

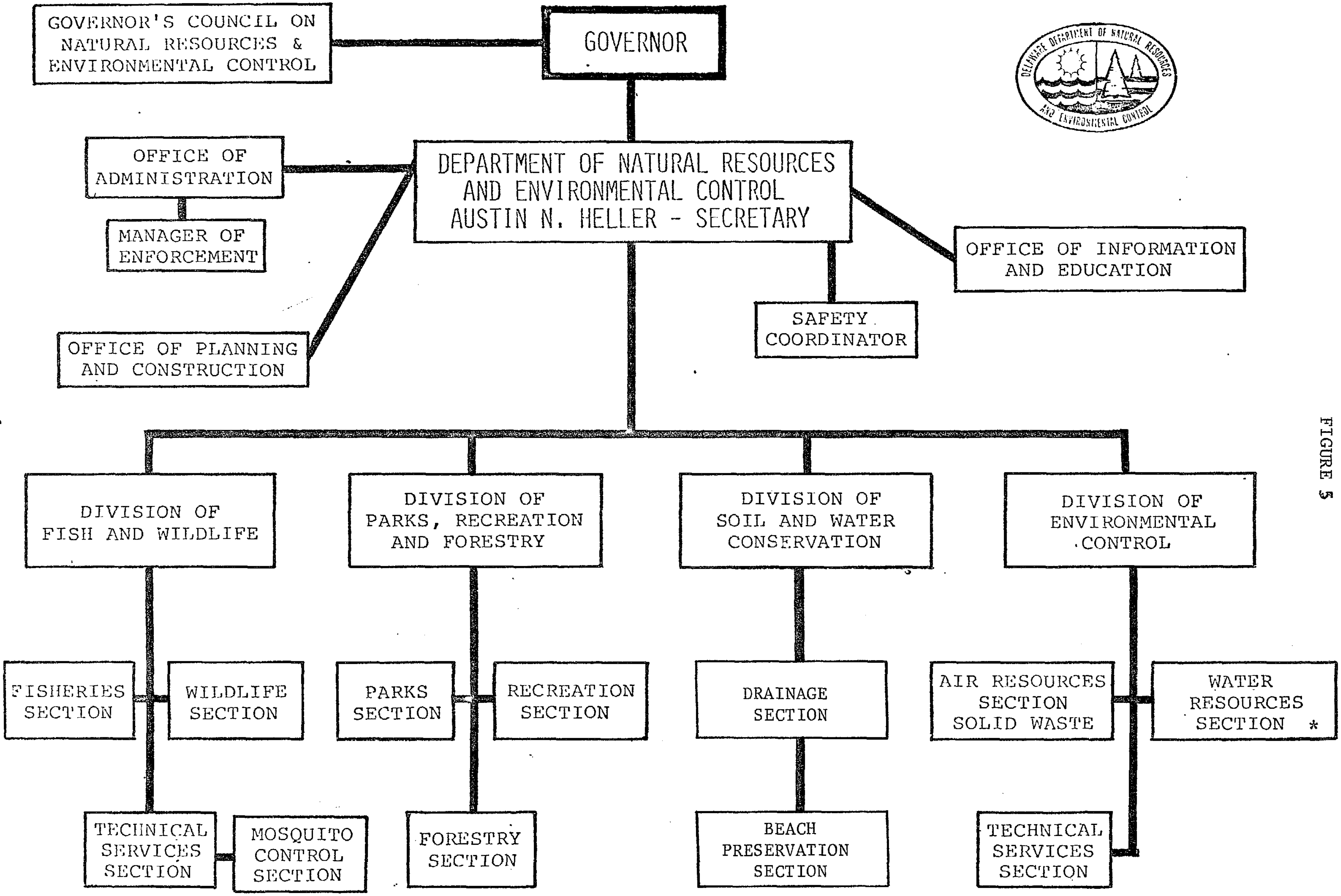
VII ORGANIZATION & GENERAL BACKGROUND

VII. Organization and General Background

The Delaware Department of Natural Resources and Environmental Control officially came into being on November 5, 1969. When the State Government was reorganized by Governor Peterson and the 125th General Assembly, the responsibilities for environmental protection were assigned to the Department of Natural Resources and Environmental Control.

This cabinet department was formed by the consolidation of five heretofore relatively independently active commissions: (1) Board of Game and Fish Commissioners, (2) Shell Fisheries Commission, (3) State Park Commission, (4) State Forestry Commission, (5) State Soil and Water Commission, and in addition the Recreation Advisory Council continues to provide services to the Department. The Water and Air Resources Commission retains its semi-autonomous status. Its staff has been consolidated into the Division of Environmental Control. However, it becomes apparent, even to the most casual observer, that there is a strong interrelationship in terms of ecological balance and environmental impact among these several areas of responsibility. The actions of one can vitally affect another.

Accordingly, under the cabinet form of government, these functions were brought together to form a single multi-disciplined team working together toward the goal of high environmental quality (Figure 5). Any proposed action affecting one group is assessed by all of the others in terms of possible impact. Technical specialists review every facet of proposals to avoid costly, and sometimes almost irretrievalbe mistakes.



* Design and engineering for beach preservation project.

FIGURE 5

With the benefit of technical analysis, scientific studies, engineering projections and staff consultations the Secretary of Department of Natural Resources and Environmental Control is enabled to make decisions protecting the best long-term interests of the people of the State of Delaware.

There are 254 full-time staff members within the Department, with summer employment increasing this number to 508. The total operating budget for Fiscal Year 1973 (State and Federal funds) is $12,772,063; capital improvement monies for Fiscal Year 1973 amount to $17,541,067.

DNREC, Grants and Federal Aid Projects

Existing Department grants and Federal aid projects cogent to this study include the following:

Agency	Amount
Delaware River (DRBC)	$ 45,000
Delaware Estuary (State/DRBC)	20,000
Federal Water Grant	86,000
Federal Air Grant	234,314
National Marine Fisheries Service	18,000
Capital Improvements to Shellfish Beds	50,000
University of Delaware (Sea Grant)	11,000
Solid Waste Demonstration Plant (EPA)	9,000,000
Total Outside Funding	$ 9,464,314

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VIII. REFERENCES

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APPENDIX I

BIOGRAPHICAL SKETCH OF PRINCIPAL INVESTIGATORS AND ADVISORY PERSONNEL

BIOGRAPHICAL SKETCH

Harry W. Otto
Engineer Manager, Technical Services Section, Delaware Department of Natural Resources and Environmental Control

Education
Muhlenberg College - B. S. in Chemistry, 1955
Pennsylvania State University - M. S. in Physical Chemistry, 1958
Pennsylvania State University - Ph. D. in Physical Chemistry, 1961

Professional Experience
State of Delaware, Division of Environmental Control, Department of Natural Resources and Environmental Control, Dover, Delaware - Engineer Manager, Technical Services Section (Air and Water), 1971 - Present.
Advisor (Industry and the Federal Government), Air Pollution Projects, 1967 - Present
Project Consultant (Federal Government), Air Pollution Abatement; Training Lecturer; Biological/Limnological Model Development, 1970 - present.
Esso Research and Engineering Company - Researcher: Automotive Emission Control, Atmospheric Chemistry, Pollution Effects on Agriculture, Analysis of Trace Constituents, 1966 - 1971.
Researcher: Diesel Pollution Problems, 1965 - 1966.
Researcher: Development and Testing of Exotic High Energy Propellants, 1961 - 1965.
Pennsylvania State University - Research (under a grant from the Atomic Energy Commission), Investigated the Reactions and Properties of Organosilicon Compounds, 1952 - 1955.
Pennsylvania State University - Instructor, Physical Chemistry, 1955 - 1956.
Pennsylvania State University - Fellow (Atomic Energy Commission), 1956 - 1961.
Barrett Division of Allied Chemical Corporation - Chemist, 1956

Professional Societies
American Chemical Society
American Association for the Advancement of Science
Air Pollution Control Association
Sigma Xi (Honorary-Research)
Pi Mu Epsilon (Honorary-Mathematics)
Phi Lambda Upsilon (Honorary-Chemistry)

Publications
Dr. Otto is the author of numerous scientific/technical publications and presentations in the field of atmospheric chemistry, air pollution monitoring, trace analysis, biological impact of air pollutants, and air pollution control.

BIOGRAPHICAL SKETCH

Charles A. Lesser
Manager, Technical Services Section, Division of Fish and Wildlife, Delaware Department of Natural Resources and Environmental Control.

Education
University of Rhode Island - B. S. in Zoology, 1964.
University of Delaware - M. S. in Entomology and Applied Ecology, 1966.

Professional Experience
State of Delaware, Division of Fish and Wildlife, Department of Natural Resources and Environmental Control, Dover, Delaware - Manager, Technical Services Section, 1970 - Present.
State of Delaware, Division of Fish and Wildlife, DNREC - Game and Fish Biologist, 1966 - 1970.
Delaware State College, Dover, Delaware - Instructor, Ornithology, 1969.
U. S. Fish and Wildlife Service, Predator and Rodent Control Section, Newark, Delaware - Wildlife Technician, 1962, 1963 and 1964.

Professional Societies
Phi Sigma Society
Sigma Xi

Publications
Mr. Lesser is author or co-author of numerous Department studies involving wildlife inventories, aquatic vegetation surveys, fishway and Black Duck evaluations, marine fisheries surveys, and oyster monitoring of the Delaware River estuary.

BIOGRAPHICAL SKETCH

N. C. Vasuki
Manager, Water Resources, Division of Environmental Control, Delaware Department of Natural Resources and Environmental Control.

Education
National Institute of Engineering, University of Mysore, India - Bachelor of Engineering (Civil), 1959
University of Delaware - M.S. in Civil Engineering, 1963

Professional Experience
State of Delaware, Division of Environmental Control, Department of Natural Resources and Environmental Control, Dover, Delaware:
Manager, Water Resources, Division of Environmental Control, 1971 - present.
Manager, Technical Services, Division of Environmental Control, 1970 - 1971.
Assistant Director, Water and Air Resources Commission, 1968 - 1970.

Technical Advisory Affiliations
Consultant to local and state agencies, industry, and consulting engineers regarding water pollution control problems.
Member of the National Industrial Wastes Committee, Water Pollution Control Federation.
Technical Advisory Committee member, Delaware Estuary Comprehensive Study. (1961-1967)
Policy Advisory Committee member, Delaware Estuary Comprehensive Study. (1965-1967)
Water Quality Advisory Committee member, Delaware River Basin Commission.
Member, Delaware River Basin Commission, Basinwide Pollution Planning Task Force.
Member, Governor's Delaware Bay Oil Transport Committee.

Professional Societies
National Society of Professional Engineers
Water Pollution Control Federation
American Water Works Association
Sigma Xi
American Men of Science
Who's Who in the East

Publications
Vasuki, N. C., "Evaluation of the Change in Water Quality of the Brandywine Creek Over a Period of Twenty Years." Symposium on Stream Flow Regulation for Quality Control, Cincinnati, Ohio, April 1963.

Vasuki, N. C., "A Dark Field Photomicrographic Method for Measuring Velocity Profiles." Library of the University of Delaware. (Masters Thesis, Civil Engineering Department, 1963).

Frey, K. P. H., and Vasuki, N. C., "Tests on Flow Development in Diffusers." Symposium on Fully Separated Flows, A. S. M. E. Fluids Engineering Conference, Philadelphia, Pennsylvania, May 1964.

Bryson, J. C., and Vasuki, N. C., "The Role of Instrumentation in a Water Pollution Control Program." Twenty-fifth International Symposium on Automation in Analytical Chemistry, New York, Frankfurt, and London, 1964.

Vasuki, N. C., "Effects of Water Pollution." State Planning Conference, University of Delaware, Newark, Delaware, June 1965.

Frey, K. P. H., and Vasuki, N. C., "Flow Stability for Two Dimensional Cusp Devices." Third National Symposium of Fluid Amplifiers, Harry Diamond Laboratories, U. S. Army, Washington, D. C., October 1965.

Frey, K. P. H., in collaboration with Vasuki, N. C., "Detached Flow and Control." Newark, Delaware, February, 1966. A reference book on Detached Flow Phenomenon.

Vasuki, N. C., and Sabis, W. R., "In-Plant Control of Poultry Waste Discharges." First Mid-Atlantic Industrial Waste Conference, University of Delaware, Newark, Delaware, November 1967.

Bryson, J. C., and Vasuki, N. C., "Water Pollution - State Officials' Viewpoint." Sixth Annual Liberty Bell Corrosion Course, Drexel Institute of Technology, September 1968.

Heller, A. N., Bryson, J. C., and Vasuki, N. C., "Some Applications of Remote Sensing in Atmospheric Monitoring Programs," Symposium on Remote Sensing of the Chesapeake Bay, NASA, Wallops Island, Virginia, 1971.

Vasuki, N. C., "Water Quality Limitations in Delaware", Proceedings of the Fourth Mid-Atlantic Industrial Waste Conference, University of Delaware, Newark, Delaware, 1971.

BIOGRAPHICAL SKETCH

John C. Bryson
Director, Division of Environmental Control, Delaware Department of Natural Resources and Environmental Control

Education

Western Carolina College - B.S. in Mathematics and Chemistry, 1958.
Syracuse University - M.S. in Sanitary Engineering, 1961.

Professional Experience

State of Delaware, Division of Environmental Control, Department of Natural Resources and Environmental Control, Dover, Delaware:
- Director, Division of Environmental Control, 1970 - present.
- Executive Director, Delaware Water and Air Resources Commission, 1966-1970.
- Director, Delaware Water Pollution Commission, 1964 - 1966.
- Acting Director, Delaware Water Pollution Commission, 1963 - 1964.
- Assistant Director of Laboratories, Delaware Water Pollution Commission, 1961 - 1963.
- Water Pollution Chemist, State of North Carolina, 1958 - 1959.

Professional Societies

Professional Engineer, State of Delaware
National Society of Professional Engineers
International Association of Water Pollution Research
Association of State and Interstate Water Pollution Control Administrators
Maryland - Delaware Waste Water Operators Association
Chesapeake Water Pollution Control Association

Honors

President - 1971, Chesapeake Water Pollution Control Association

Publications

Bryson, J., "Color Measurement." Seventh Ontario Industrial Waste Conference, Honey Harbour, Ontario, Canada (1960).

Bryson, J., "Hancock Air Force Base Oxidation Pond Research Studies." Syracuse University Research Institute, Syracuse, New York (1961).

Bryson, J., "How Efficient are Oxidation Ponds." Wastes Eng., 32, 3 (1963).

Bryson, J., "The Role of Instrumentation in a Water Pollution Control Program." Twenty-Fifth International Symposium on Automated Analytical Chemistry, Germany and the United States (1964).

Bryson, J., "Automated Analytical Instruments Play Role in Pollution Control." Water and Wastes Eng., 3, 10 (1966).

BIOGRAPHICAL SKETCH

Darrell L. Louder
Director, Division of Fish and Wildlife, Delaware Department of Natural Resources and Environmental Control.

Education

Southern Illinois University - B. S. in Zoology, 1955
Southern Illinois University - M. S. in Zoology, 1957

Professional Experience

State of Delaware, Division of Fish and Wildlife, Department of Natural Resources and Environmental Control - Director, 1972 - present.
North Carolina Wildlife Resources Commission, Division of Inland Fisheries:
- Assistant Chief, 1970 - 1971
- Supervisor of Fisheries, 1965 - 1970
- Limnologist, 1964 - 1965
- Fishery Management Biologist III, 1962 - 1963
- Fishery Management Biologist II, 1957 - 1962

Illinois Department of Conservation, Carbondale, Illinois - Assistant Fishery Biologist, 1952 - 1955.
Pet Milk Company, Greenville, Illinois - Laboratory Assistant, 1951 and 1952.

Consultant Activities

Management of the Ecological Habitats of Animals; Animal Exhibit Design, North Carolina Wildlife Resource Commission.
Fish, Wildlife, and Mosquito Control - Television Consultant and Commentator.

Technical Advisory Affiliations

Southern Division, American Fisheries Society
American Fisheries Society
Northeastern Association of Game, Fish and Conservation Commissioners
Atlantic Waterfowl Council

Professional Societies

American Fisheries Society
Southern Division - American Fisheries Society
International Association of Game, Fish and Conservation Commissioners
Delaware Academy of Science
Northeastern Association of Game, Fish and Conservation Commissioners
Atlantic Waterfowl Council

Publications

Mr. Louder has had published more than 40 scientific and technical articles dealing with fish and wildlife research and management and is considered an expert in this field.

BIOGRAPHICAL SKETCH

Austin N. Heller
Secretary, Delaware Department of Natural Resources and Environmental Control.

Education

Johns Hopkins University, A. B., Chemistry, 1938
Johns Hopkins Graduate School of Engineering, 1939
Iowa State University, M. S., Sanitary Bacteriology-Chemical Engineering, 1941

Academic Experience

Adjunct Associate Professor of Environmental Health, Columbia University, September 1966 - 1970.
Adjunct Professor, Environmental Engineering, The Cooper Union School of Engineering & Science, September 1966 - 1967.
Research Associate, Department of Civil Engineering, New York University College of Engineering, 1946 - 1948.
Advisor to Program Directorate, Sea Grant Program, University of Delaware, 1971 - Present

Industrial Experience

Allied Chemical Corporation, New York City, Supervisor, Industrial Waste Development Section; Coordinator, Long Range Planning, Research and Development Department (Barrett and Plastics Division) 1948 - 1961.
Wallace and Tiernan Company, Bellville, New Jersey, Chemist - Bacteriologist, January 1942 - June 1942.

Governmental Experience

Secretary, Department of Natural Resources and Environmental Control, Dover, Delaware - Appointed March 2, 1970.
New York City Department of Air Resources, Commissioner - Appointed July 1, 1966 - 1970.
United States Public Health Service, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio. Deputy Chief, Technical Assistance Branch, Division of Air Pollution Control, 1961 - 1966.
Member of Governor's Committee on Power Plants and the Environment (Chesapeake Bay), 1970 - 1972.
Member of Governor's Task Force on Marine and Coastal Affairs, Delaware, 1970.

Technical Advisory Affiliations

American Society of Mechanical Engineers, Chairman - Task Group, 1959 Preparation of "Guide to Research in Air Pollution," published in 1961.
Joint Study Committee, Manufacturing Chemists' Association and U. S. Public Health Service - "Emissions from Selected Chemical Processes" - member of Steering Committee. Principal representative of U. S. Public Health Service 1965 - 1966.
American Institute of Chemical Engineers, co-chairman of the Symposium of Interrelationship of Air and Water Pollution Problems, May 1966, Columbus, Ohio.

Consultant Activities

Consultant to Surgeon General, Belgian Government, 1965.
Royal Commission for Air Purification, Government of Sweden, 1965.
Permanent U. S. Delegate, O.E.C.D., Scientific Division - Air Pollution, Research Survey Techniques Group, Paris, France, 1965 - present.

Professional Societies

American Association for the Advancement of Science, Air Pollution Control Association - Board of Directors, 1958 - 1960; 1967 - 1970
American Chemical Society
American Institute of Chemical Engineers
American Public Health Association, elected Fellow in 1968
American Water Works Association, Life member
Water Pollution Control Federation
American Academy of Environmental Engineers, Diplomate, June 1969
New York State Society of Professional Engineers
National Society of Professional Engineers
American Institute of Chemists, elected Fellow in 1969

Honors and Awards

Graduate Scholarship, Johns Hopkins University, 1938-39
Research Fellowship, Iowa State University, 1940-41
American Society of Mechanical Engineers' Spring Round-up Engineering Award for Outstanding Leadership, 1967; Metropolitan - New York Chapter
Princeton University - Member of Advisory Council, Department of Chemical Engineering, July 1967 to present
Annual Award, New York State Society of Engineers, 1968; Kings County Chapter
Humanitarian Award, Children's Asthma Research Institute and Hospital, April 1969
Diplomate, American Academy of Environmental Engineers, June 1969
Leaders in American Science, Vol. VIII, 1968-1969; Engineers of Distinction, 1970
Who's Who in America, 1972
Engineering Index - Board of Trustees, April 1969 - 1972

Publications

Secretary Heller is author or co-author of more than 40 scientific articles and patents. His work encompasses a rather broad spectrum, including bacteriological and statistical analyses of water and wastewater, industrial waste processes and management, and over 15 articles on air pollution causes, monitoring, and management.

A sampling of Secretary Heller's work follows:

Heukelekian, H., and Heller, A. N., "Relation Between Food Concentration and Surface for Bacterial Growth." Journal Bacteriology (October 1940).

Heller, A. N., "Proposed Plan for Water Main Sterilization." Journal American Water Works Association (December 1943).

Heller, A. N., "Prevention of Stream Pollution by the Treatment or Elimination of Wastes at their Source" 1955 Industrial Wastes Forum: The Organic Chemical Industry, Sewage and Industrial Wastes (May 1956).

Heller, A.N., and Reiter, W.M., "Recovery of Phenolics from Tar Distillation Waste Liquors via Solvent Extraction." 12th Purdue Industrial Waste Conference (May 1958).

Fertig, J. W. and Heller, A. N., "The Application of Statistical Techniques to Sewage Treatment Processes." Biometrics (June 1960).

Heller, A. N., "Methods of Evaluation Socioeconomic Effects of Air Pollution." Proc. International Research Conference on Atmospheric Emissions from Sulfate Pulping, U. S. Public Health Service (April 1966)

Johnson, K. L., Dworetsky, L. H., and Heller, A. N., "Carbon Monoxide and Air Pollution from Automobile Emissions in New York City."Science, Vol. 160, 67 (April 1968)

Gregor, Harry P., Heller, A.N., and Mark, Herman F., "Polymer Science in the Prevention of Air Pollution." Annals of the New York Academy of Science, Vol. 155, Art. 2 (January 1969).

Heller, A.N., "Governments Can Manage Air Pollution Control." National Civic Review (January 1971).

Solvent Dephenolization of Aqueous Solutions. Canadian Patent 586,371 - November 3, 1959.

Heller, A. N., "Role of the Scientist in Urban Ecology," Transactions of the New York Academy of Science, (June 1968)

APPENDIX II

PREVIOUS DELAWARE ESTUARY STUDIES

Previous Delaware River - Bay Studies

1. First Annual Report, 1949 - 1950
2. Second Annual Report, 1950 - 1951
3. Survey of Pollution and its effects upon the streams within the Broadkill Drainage Basin 1951
4. Survey of pollution and effects, Mispillion River, 1951
5. Survey of pollution and effects upon Bunting's Branch Bishopville Prong and Drainage Basin
6. A comprehensive study of pollution on Red Clay Creek
7. Third Annual Report, 1951 - 1952
8. A study of the accumulation and distribution of Iron waste discharges in Delaware River
9. Fourth Annual Report, 1952 - 1953
10. A comprehensive study of pollution on Brandywine River, 1954
11. Fifth Annual Report, 1953 - 1954
12. A comprehensive study of pollution in Indian River
13. Sixth Annual Report, 1954 - 1955
14. Seventh Annual Report, 1955 - 1956
15. Technical Report Investigation of Water Quality in lower Delaware River Parts I and II
16. A comprehensive study of pollution and its effects on waters within Nanticoke River Basin
17. Water Pollution Commission 8th Annual Report
18. Water Pollution Commission 9th Annual Report
19. Water Pollution Commission 10th Annual Report
20. Water Pollution Commission 11th Annual Report

21. Water and Air Resources Commission First Annual Report

22. Water and Air Resources Commission Second Annual Report

23. Water and Air Resources Commission Third Annual Report

24. Water and Air Resources Commission Guidelines for Septic Tank Installation

25. Ambient Air Standards for Sulfur Dioxide and Particulate Matter

26. Implementation Plans for Oxides of Sulfur

27. Report on wastes produced from Delaware Chicken Packing Plants

28. St. Jones River Report

29. Estuary model tests expedite prototype studies of pollution

30. Oxidation Pond Studies on Plant Wastes from Poultry

31. Interstate Water Resources Survey 1959

32. Availability of Ground Water, Eastern Sussex

33. Availability of Ground Water, Western Sussex

34. Availability of Ground Water, Kent County

35. Availability of Ground Water, Chesapeake and Delaware Canal

36. Water and Air Resources Management

37. What Happened in Delaware?

38. Oil Pollution in Delaware

39. Role of Instrumentation in Water Pollution Control

40. Delaware River Estuary Comprehensive Study

41. Some applications of remote sensing in atmospheric monitoring programs

42. Water Quality Limitations in Delaware

43. Dispersion Studies on the Delaware River

44. Dispersion Studies on the Delaware River model and potential application toward stream purification capacity evaluations

45. deSylva, D.P. Marine Sport Fishing Investigations, 7/1/58-6/30/59

46. deSylva, D.P., F.A. Kalber, and R. Seguin, 1960
Section 1. Preliminary Investigations on Shore Zone Fishes of Delaware Bay Area, deSylva and Kalber
2. Investigation of Fishes Captured By Trawls in Delaware Bay area, deSylva and Kalber
3. Hydrographic Studies in Delaware River Estuary, deSylva & Kalber
4. Pilot Study on Nutrients in Delaware River Estuary, Kalber
5. Bluefish Pepsin, Kalber
6. Racial Investigation of Grey Sea Trout, Seguin
7. White Marlin Fishery of Middle Atlantic fight, deSylva

47. deSylva, D.P. 1961, Racial Status of Juvenile Striped Bass in Delaware Bay Estuary

48. deSylva, Kalber & Shuster, 1962 Fishes in the Shore Zone and Other Areas of Delaware River Estuary

49. Miller, L.W. 1963, Growth, Reproduction and Food Habits of White Perch in Delaware River Estuary

50. Daiber, F.C., Role of Saltmarsh in the Lives of Saltwater Fishes

Warlen, S.M., Some Aspects of the Life History of Cyprmodon variegatus in Southern Delaware

Schmelz, G.W., A Natural History Study of the Mummichop, Fudulus heteroclitus, in Canary Creek Marsh

51. Daiber, continued, F-13-R-6 (Daiber, 1964)
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